

PROJECT-SPECIFIC CALIBRATION AND ESTABLISHMENT OF DETECTION AND QUANTIFICATION LIMITS FOR THE USE OF PORTABLE XRF (pXRF) IN THE TRACE-ELEMENT ANALYSIS OF GEOLOGICAL SAMPLES

pXRF-ANALYSIS OF GEOLOGICAL SAMPLES

Portable X-ray Fluorescence analysis (pXRF) is currently being used for the chemical characterisation of a large variety of materials, i.e. geological, archaeological and forensic samples, alloys, ... The technique is able to detect and quantify the presence of trace, minor and major elements in these materials at concentration levels ranging from part-per-million (ppm) up to weight percentage. However, different modes of operation (instrument settings) are often required for reliable analysis at different concentration levels. For example, optimum factory calibration and instrument settings for most minor and trace elements in geological samples are provided as a “soil-mode” of operation. This “soil-mode” uses a Compton-normalisation procedure in order to convert obtained spectrometric intensity readings to concentration values that are given as “read-outs” by the pXRF-instrument.

IMPORTANCE OF CORRECTLY DETERMINED DETECTION AND QUANTIFICATION LIMITS AND OF EMPIRICAL CALIBRATION

Optimum detection limits in “soil-mode” given by the manufacturers are typically lower than 20 ppm for elements with atomic number larger than 22 (i.e. from titanium onwards in the Periodic Table). Such optimum detection limits have been established using spiked SiO₂-based standard materials devoid of any interfering elements. However, real-life samples often have complex matrices, especially in the case of geological materials (rocks, soils). This implies that chemical matrix-effects such as spectral interferences (peak overlaps) and enhancement or absorption phenomena will likely exist and will influence the detection capabilities for the various elements of interest.

The detection limit for a specific element given by the pXRF-instrument is determined

as the concentration (resulting from the Compton-normalisation procedure) corresponding to three times the standard deviation of the measured signal for that element. Measured signals larger than three times its standard deviation, are reported as “above detection limit” and a concentration value is given as “read-out”. However, our experience has shown that *real*, empirically-defined detection limits using well-defined geological samples (analysed multiple times by conventional laboratory-based techniques) can frequently be up to three times higher than those estimated by the pXRF instrument (illustrated for Ni in Figure 1; comparable issues are noted for other elements such as As, Cr, Cu, etc).

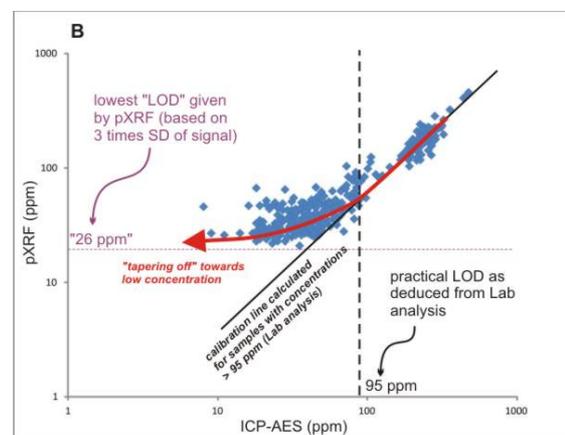
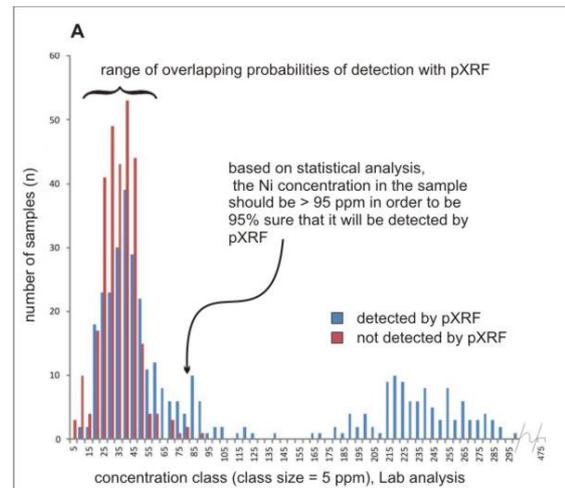


Figure 1. Importance of the use of practical, project-specific detection limits (LOD's) for use of the Ni concentration as a geochemical tracer (for alteration mapping, lithological discrimination) in fine-grained (altered) metasedimentary and metavolcanic rocks in a greenstone-hosted gold exploration project. Optimum LOD's for Ni are often indicated to lie below 20 ppm by pXRF manufacturers.

A. Histogram of the Ni concentration in 670 pulp core samples from various encountered lithologies as determined by laboratory-based four-acid digestion ICP-AES analysis. The histogram shows a differentiation between those samples where Ni was reported as "above LOD" and "below LOD" in subsequent pXRF analysis of the returned sample pulps. This pXRF-related "LOD" for individual samples is classically based on 3 times the standard deviation of the obtained signal. The figure indicates that for concentrations between 15 and 50 ppm in the analysed lithologies, one was as likely to obtain a pXRF-reading "above LOD" as "below LOD". Detailed analysis showed that this was independent of lithology.

B. Comparison between laboratory determined Ni concentration and the corresponding concentration value obtained by pXRF analysis (value corrected by external calibration of the pXRF-analysis using a range of certified reference materials covering the same lithological types of rocks as encountered in the drilling project). The pXRF results thus all yielded as "above LOD" by the instrument and could erroneously be interpreted as a reliable concentration of Ni in the samples. However, a clear "tapering-off" of the pXRF results can be seen at low concentrations. Statistical analysis demonstrated that practical limits of detection for Ni in this project should be around ~95 ppm. A sample having a concentration below this value cannot be reliably analysed by pXRF in this project (at least with the particular pXRF-apparatus and set-up used in this study). For this particular project, it meant that 67 % of samples for which a pXRF-reading "above LOD" was obtained by the apparatus were to be discarded.

This implies that uncorrected pXRF results ("read-outs") close to the *real* detection limits in these samples are unreliable and that empirical detection and calibration strategies have to be applied in order to obtain meaningful quantitative results.

For many geological and environmental applications, such as the identification of heavy metal pollution in soils or for lithological characterisation of rock samples, reliable trace element detection and quantification is essential. Therefore, these applications require the estimation of

project-specific detection and quantification limits, as well as the establishment of an empirical (external) calibration of the pXRF readings using a range of well-known calibration materials with matrices that closely match those of the samples to be analysed.

When such empirical detection and quantification limits are correctly determined and applied, and empirical calibration is properly made, pXRF is capable of producing analytical results on trace element concentrations that are as good as those of conventional quantitative laboratory analysis (e.g. acid-digestion coupled with ICP-AES or ICP-MS analysis) in terms of reproducibility (precision) and trueness (accuracy).

GF CONSULT PROVIDES TRAINING ON THE USE OF PORTABLE XRF AND THE PROPER INTERPRETATION OF THE ANALYTICAL RESULTS OBTAINED

GF Consult bvba has installed and optimised field laboratories for portable XRF equipment for several companies working in a variety of geological settings. Moreover, we provide training in the use of this equipment, in sample preparation protocols and in proper data reduction.

For more information on how we can assist you in valorising your field exploration programs by using pXRF, please do not hesitate to contact us at following address :



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